The Statistical Mechanical Distribution Functions

1 Stirling's Formula

We will need an approximation for the factorial, for large n. This is given by (see Boas, p. 472; for a derivation, see the text by Arfken, for example):

$$n! \approx n^n e^{-n} \sqrt{2\pi n}.\tag{1}$$

For the logarithm, this becomes:

$$\ln(n!) = n \ln n - n + \ln(n) + \ln(2\pi)$$
(2)

So the accuracy of the approximation which we used in class requires that $\ln n$ be large compared to 1. For some particular cases: $\ln(200!) = 863.232$. Keeping all the terms gives the same result to six significant figures. But keeping only the first term gives: 1059.66. So it is off by about 15%. This is to be expected, since $\ln(200) \approx 5$.

2 The Spirit of Statistical Mechanics

The basic idea, of Gibbs, Maxwell, and Boltzmann, was that all possible states of a system are equally likely, and that most states, by an exponentially large amount, look like some typical state.

If we ignore statistics, we arrive at the Boltzmann distribution. The idea is to suppose that the energy can take on some discrete set of values, E_1, E_2, \ldots If one has N particles, these can be distributed in various ways among these states. Suppose that there are n_1 particles with energy E_1 , n_2 with energy E_2 , etc. Now ask how many ways can we distribute N particles among these different energies. Start with the first. There are N choices of particles to put first into the first box; N - 1 to put second, and so on. This gives

$$\frac{N(N-1)\dots(N-n_1+1)}{n_1!}$$
(3)

where we have to divide by n_1 ! to compensate for the fact that the order in which we put particles in the box doesn't matter.

We have a similar factor for E_2 , E_3 , etc. For E_2 , for example, we have a factor:

$$\frac{(N-n_1)(N-n_1-1)\dots(N-n_1-n_2+1)}{n_2!}.$$
(4)

So the total number of possibilities is proportional to:

$$P(\{n_i\}) = \frac{N!}{\prod n_i!} \tag{5}$$

We want to maximize this subject to the requirements that

$$\sum n_i = N \qquad \sum n_i E_i = E \tag{6}$$

where we are assuming that the total number of particles and the total energy are fixed.

It is easier to study the logarithm of P. So we want to maximize:

$$W = -\sum \ln(n_i!) - \alpha(\sum n_i - N) - \beta \sum (n_i E_i - E).$$
(7)

 α and β are called "Lagrange Multipliers" (see Boas, p. 174). The main thing to note is that if we differentiate W with respect to α and β (and set the derivative to zero), we enforce the constraints on the total number of particles and the energy.

Let's use Stirling's formula to write W as

$$W = \sum (-n_i \ln n_i + n_i - \alpha n_i - \beta n_i E_i) + \text{terms independent of } n_i.$$
(8)

Now, for every i, we want

$$\frac{\partial W}{\partial n_i} = 0 = -\ln n_i - \alpha - \beta E_i.$$
(9)

Solving for n_i gives

$$n_i = \text{constant } e^{-\beta E_i - \alpha}.$$
 (10)

3 The Bose-Einstein and Fermi-Dirac Distributions

The main difference here is that one must keep track of statistics. The results for P again involve various factorials; maximizing W gives the distribution functions.

I will put on the website shortly a derivation of the Bose-Einstein and Fermi Dirac distributions from a textbook.